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Determination of Lead and Cadmium in Fish and Clam Tissue by Atomic Absorption Spectrometry with a Molybdenum and Lanthanum Treated Pyrolytic Grahite Atomizer

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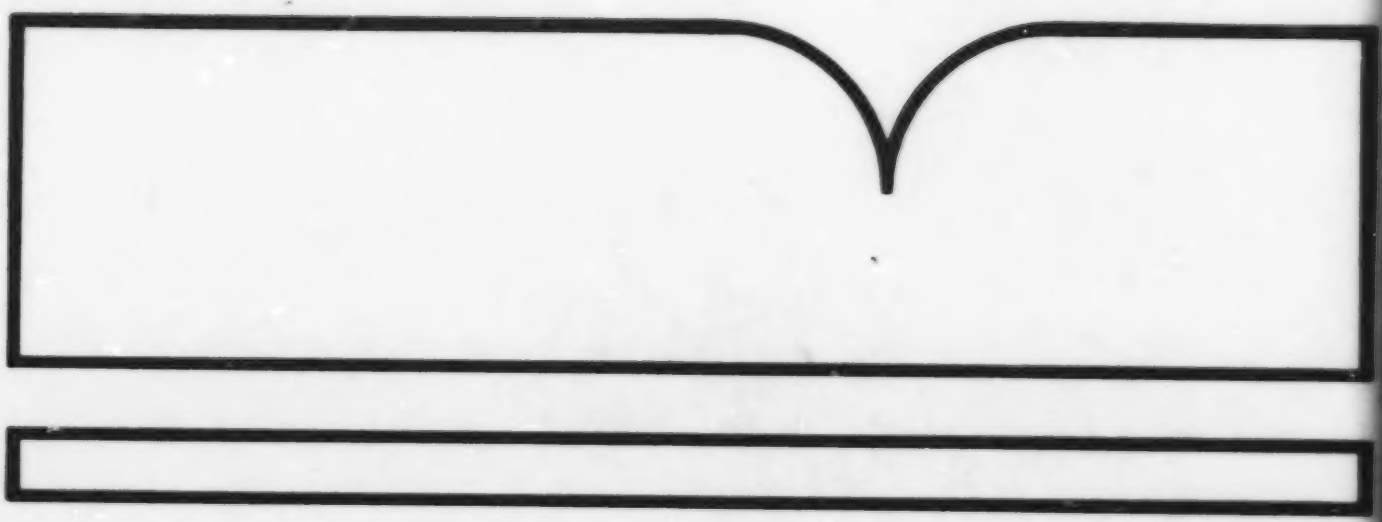

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16. ABSTRACT

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Determination of Lead and Cadmium in Fish and Clam Tissue by Atomic Absorption Spectrometry with a Molybdenum and Lanthanum Treated Pyrolytic Graphite Atomizer

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A molybdenum and lanthanum treated pyrolytically coated graphite tube is employed for the furnace atomic absorption spectrometric determination of lead and cadmium directly in nitric–perchloric acid tissue digests. Lanthanum tends to promote the formation of a smooth lead atomization peak for aid in peak quantitation. Both molybdenum and lanthanum help reduce chemical interference and interference from uncompensated background signals during analyte atomization. Under typical conditions, the average analytical recoveries are within the 90–110% range for both lead and cadmium, and peak height reproducibility is about 2–3% when working sufficiently above detection limits. Accuracy of the method is assessed by analyzing the NBS SRM 1577 bovine liver standard and performing alternate determinations by anodic stripping voltammetry.

Furnace atomic absorption spectrometric (FAAS) determinations of lead and cadmium in fish tissue digests can be beset with chemical and background interferences due to various matrix components. Several workers have demonstrated that the presence of certain inorganic salts can give rise to various interferences (*1–8*). Digests contain significant concentrations of various salts and although adequate results may be obtained if the method of standard additions is used, digests must be diluted sufficiently to reduce the interfering matrix concentration, with a corresponding sacrifice in detection limit. To avoid these problems, the analyte is sometimes extracted from the matrix as a metal complex into an organic solvent (*9, 10*). Such procedures can be valuable for some matrices, but an obvious disadvantage is more labor intensive sample handling with the additional inherent possibility for inadvertent sample contamination.

Use of various organic and inorganic reagent additions to samples has also been reported to help chemically modify and reduce interferences from various substances (*1–3, 5–7*). One reagent, ammonium nitrate, is known to significantly reduce some interfering salt matrices prior to the atomization step (*11*). Other improvements in various analytical procedures have focused more directly on use of different furnace designs and materials for atomization, such as pyrolytic carbon deposition which can extend the lifetime of a graphite tube and reduce carbide formation, compared to a conventional graphite tube (*12*). Furthermore, it has been indicated that coating or impregnating tubes with certain metal carbides (*3, 5, 7, 8, 13–15*) and atomizing at near constant temperature (*6*) or constant temperature (*16*) conditions can significantly affect tube life, background absorption, or the efficiency of atomization of the metal. As often discussed by previous workers, one mechanism of chemical interference reduction naturally involves shifting the equilibrium (with chemical reagents or electrothermal heating techniques) such that formation of analyte atoms at a single appearance temperature is favored over the formation of molecular species. These studies are generally practical reflections of such considerations.

Since none of the work involving metal-carbide treated tubes has been reported for the determination of both lead and cadmium in fish tissue, a particularly difficult matrix, work was undertaken to examine the possible application of these approaches. Although several elements such as zirconium, hafnium, niobium, tantalum, molybdenum, and tungsten form stable interstitial carbides, initial studies suggested that using treatments of molybdenum or lanthanum on the atomizer and the addition of ammonium nitrate to the sample may allow the direct sequential determination of lead and cadmium concentrations in nitric–perchloric acid fish tissue digests with a relatively low acid content. Desirable characteristics of such an analytical method include: (1) production of a smooth and easily quantifiable atomization peak, (2) minimal chemical and background interferences, (3) applicability to more than one element, (4) acceptable reproducibility and accuracy, (5) minimal sample manipulation and operator time, and (6) acceptable long term instrument calibration stability. This paper reports a new analytical method for lead and cadmium possessing such attributes in which both molybdenum and lanthanum are used to treat the atomizer.

EXPERIMENTAL

Apparatus. The atomic absorption equipment (Perkin-Elmer) consisted of a Model 305B spectrophotometer equipped with a deuterium arc background corrector, a Model HGA-2100 furnace (with ramp accessory), a Model AS-1 autosampler, a Model UDR-2 for storage of the transient atomization peak, and a Model 56 recorder. For some measurements, a Perkin-Elmer Model 403 spectrophotometer was used. A H_2 hollow cathode lamp (Oriel) was used for some background signal measurements. The spectral source for cadmium was an electrodeless discharge lamp and for lead it was either a hollow cathode lamp or an electrodeless discharge lamp. The background corrector was routinely employed

and care was taken to ensure optimal coincidence of the sample and reference beams in the sample compartment.

The electrode and instrumentation used for determinations by anodic stripping voltammetry (ASV) have been previously described (*17*).

Computer-Assisted Data Acquisition and Reduction. The Model UDR-2 was used to store a voltage level which was proportional to the peak height of the atomization signal. The range was adjusted so that 1 absorbance unit corresponded to 1 V at its output (pins 9 and 14 of P/J4, schematic # 290-0218-E). The output from the UDR-2 was input to the inverting input of an amplifier-summing circuit (*18*) which was set to unity gain. The base-line voltage from the 1-V spectrophotometer output was input through a 10-kΩ resistor to the inverting input of the summing amplifier. Therefore, after atomization, the output voltage of the summing amplifier was the difference between the peak voltage and the post-atomization base-line voltage. This voltage difference output was usually sampled for 3 s by a Model 18562A remote A/D converter (8-Hz max. sampling rate), associated with a Hewlett-Packard Model 3354B computer system. In this operational mode, the data system was capable of quantitating relatively rapid peak signals. The result for each peak was stored by the computer using the system's area slice method, a simple BASIC program, and a general data file (*19*). Reliability of peak determination by this method was characterized by dividing each computer determined value by the corresponding value of the peak height determined manually. The relative standard deviation of the mean ratio, calculated for ten peaks in the absorbance range of 0.3, was 0.2%; similarly, near an absorbance of 0.005, it was 9%. Remote A/D sampling was initiated at the proper time after atomization by closure of a relay actuated by a NE555 timer (Signetics). The timer was triggered during the charring cycle with a relay installed in the furnace power supply; before each atomization cycle, zero absorbance on the spectrophotometer was automatically set with a similarly installed relay (*18*). Acquired data were reduced using a computer-assisted procedure similar to that previously described for a different computer system (*18*).

Reagents. Deionized distilled water (Millipore Super Q) and chemicals of reagent grade quality or better were used throughout this study. Lead and cadmium standards (1000 mg/L) were prepared by dissolving the metal (99.99% purity) in nitric acid and diluting with deionized distilled water to volume. Stock solutions of ammonium nitrate were prepared by dissolving 50 g of NH_4NO_3 (Fisher) in water and diluting to 100 mL (50% w/v NH_4NO_3). The solution was purified by passing it through a column of 50–100 mesh Chelex 100 (BIO-RAD) in the ammonium form. Molybdenum stock solutions were prepared by dissolving 18.4 g of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Fisher) in 2 M NH_4OH and diluting to 100 mL (10% w/v or 100 000 mg/L Mo). Lanthanum stock solutions were prepared by dissolving 57 g of La_2O_3 (American Potash and Chemical) in a minimum volume of 10% v/v nitric acid and diluting to 1 L (5% w/v or 50 000 mg/L La). Lead and cadmium contamination was removed by extracting this solution with an equal volume of CCl_4 and 10^{-3} M sodium diethyldithiocarbamate.

Sample Digestion Procedure. Whole fish and clams (soft tissue) were digested using a procedure basically similar to that described by Leonard (*20*), with a few minor modifications which tended to favor a better analyte/blank ratio such as using a protective canopy and increasing the sample size to 0.6 g dry weight for each 10 mL of HNO_3 and 2 mL of $HClO_4$. After digestion was complete, the residue was dissolved and diluted with 0.2% v/v HNO_3 to either 10 or 20 mL, depending on sample size (1.2-g max.). Digests were stored until analysis in precleaned 30-mL linear polyethylene bottles (Nalgene).

Tube Preparation and Analysis Procedure. Preparation of a graphite tube consisted of four different steps. New graphite tubes were coated with pyrolytic graphite, similar to the Manning and Ediger procedure (*12*) except that a 95% Ar–5% methane gas mixture was held at a setting of 2300 °C for 25 min (0.3 g coating deposited). The injection hole was bored out to 2.4 mm. Secondly, a molybdenum treatment was performed according to Manning and Slavin (*5*) except that subsequently another atomization was made after impregnating the tube by submersion in 10% w/v molybdenum solution for 5 min under vacuum. This impregnation and atomization step was repeated again. Thirdly, a 50-μL aliquot of a lead spiked lanthanum nitrate solution (5% w/v La) was then injected and carried through the atomization cycle given for the molybdenum treatment. This step was repeated until maximum response for lead was obtained (typically 5 injections). The tube was finally conditioned by repeatedly (30–50 times) injecting and atomizing (Table I) a typical lead spiked sample (containing reagents as subsequently described) to ascertain normal reproducibility (2–3%) and constant sensitivity. After sufficient conditioning, the tube was inspected and any obstructions were removed with a stream of air.

Typical FAAS instrumental settings, given in Table I, represent approximate values which produced optimum atomization signals for this matrix. Blank, standard, and sample solutions were prepared to contain the following added components: 1% v/v $HClO_4$, 100 mg/L Mo, 500 mg/L La, 6% w/v NH_4NO_3. Calibration was made by the method of standard additions. As a matter of routine, the length of an analytical run was usually limited to 70–100 atomizations per element (longer runs may be possible) and cadmium was determined subsequent to lead on the same solutions. Although maximum tube life was not determined, it was in excess of 300 firings over the course of two consecutive days of analysis runs for this matrix. Long-term drift in standards was typically about 10% or less.

Determinations by ASV were made on digests (diluted 10-fold) using a previously reported procedure (*17*).

Table I. Typical Instrumental Parameters

Spectrophotometer Settings	
wavelength:	Pb, 217.0 nm; Cd, 228.8 nm
slit:	4 (0.7 nm)
D_2 background corrector turned on	
Furnace Settings	
dry:	120 °C, 30 s
char:	Pb, 550 °C; Cd, 400 °C; 30 s; ramp 15 s
atomize 1:	Pb, 2600 °C; Cd, 2500 °C; 5 s; ramp 4s; argon flow interrupted
atomize 2:	ramp module high temp control (2600 °C, 5 s with 50 mL/min internal argon flow)[a]
injection volume:	20 μL

[a] Furnace power supply modified to obtain this temperature setting.

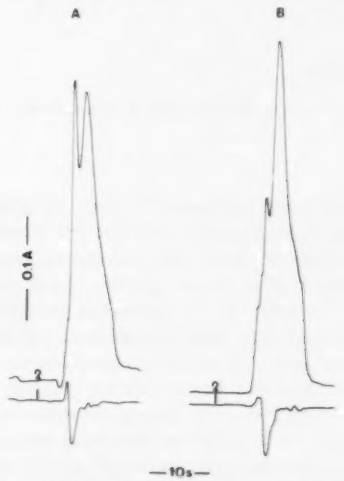

Figure 1. Lead atomization signal shape of a whole catfish tissue digest. (A) Graphite tube, (B) pyrolytic graphite tube. Curves: (1) with D_2 background correction, (2) without D_2 background correction. Added background matrix: 1% v/v $HClO_4$. Atomization settings: 2600 °C, 10 s, 4-s ramp

RESULTS AND DISCUSSION

Interference with the Atomization Signal. In the process of characterizing atomization interferences due to the presence of digest matrix components, signals for lead (Figure 1) in whole catfish digests displayed very low sensitivity and

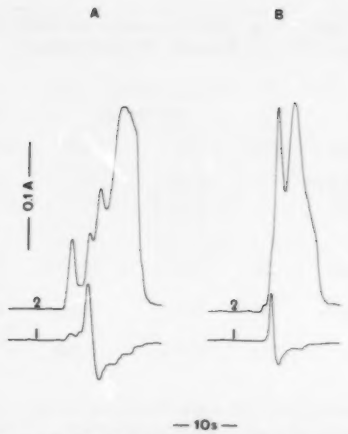

Figure 2. Lead atomization signal shape of a whole catfish tissue digest. (A) Molybdenum treated pyrolytic graphite tube, (B) molybdenum and lanthanum treated pyrolytic graphite tube. Curves: (1) with D_2 background correction, (2) without D_2 background correction. Added background matrix: (A) 1% v/v $HClO_4$, 6% w/v ammonium nitrate; (B) 1% v/v $HClO_4$, 6% w/v ammonium nitrate; 100 mg/L Mo, 500 mg/L La. Atomization settings: (A) 2500 °C, 18 s, 9-s ramp, internal gas interrupt mode; (B) 2600 °C, 10 s, 4-s ramp

large abnormal base-line deflections (using D_2 arc background correction). Analyses of five typical catfish tissue digests for possible interferents, namely calcium, magnesium, sodium, and potassium, gave mean values of 2412, 66, 192, and 382 mg/L, respectively. Digests were usually diluted 4-fold before injecting the prepared sample into the furnace. As shown in Figure 1, this behavior was present with both a graphite tube and a pyrolytically coated graphite tube. Manning and Slavin (*5*) suggested for salt matrices that some base-line abnormalities are due to residual uncompensation of the background signal. These researchers also observed similar base-line abnormalities for the nonabsorbing lead wavelength at 220.3 nm (with D_2 background correction), thus supporting such contentions. In this work, background absorbance measurements using a hydrogen hollow cathode or a lead lamp with the background corrector turned off (Figure 1) indicated similar nonspecific absorbance concurrent with the atomization signal. Addition of 6% w/v ammonium nitrate to samples or use of various degrees of ramp atomization was applied, without success, to selectively atomize the lead peak separate from the interfering matrix components.

Effect of Molybdenum and Lanthanum on Atomization. Since the interference probably originated from inorganic salts and possibly from residual organic matter, the use of a molybdenum treated pyrolytic graphite tube, ammonium nitrate addition to samples, and ramp atomization (*5*) were employed to help reduce these effects. To improve sensitivity, flow of argon was stopped during atomization and the 217.0-nm wavelength was used in all studies, since lead concentrations tended to approach detection limits. Although a much improved signal was obtained (Figure 2A), irregularities with the lead atomization peak were still evident. Unlike that for standards, the peak for a sample was not smoothly formed and its occurrence overlapped with the background curve. Shifts in the base line after the lead peak were attributed to residual uncompensation of the background signal, since base-line shifts were also observed at 217.0 nm using a hydrogen hollow cathode lamp with the deuterium arc background corrector turned on.

Irregular peak shapes with the molybdenum treated tube made peak quantitation more uncertain; thus, additional investigations were conducted to obtain improved atomization for lead. Both preliminary studies and previous reports (*3*, *7*, *13*) dealing with cadmium and lead determinations initially

Table II. Effect of Various Types of Graphite Tubes and Reagent Additions on the Percent Recovery of Lead and Cadmium in Catfish Digests

		reagents added			% recovery[a]	
no.	tube type[b]	NH_4NO_3, % w/v	Mo, mg/L	La, mg/L	Pb	Cd
1	PG	0	0	0	<10	67
2	PG	6	0	0	13	–
3	PGL	6	0	5000	54	–
4	PGM	6	0	0	93	–
5	PGM	6	100	0	94	94
6	PGML	6	0	500	93	–
7	PGML	6	100	500	94	95
8	PGML	6	100	5000	92	–

[a] Spike concentrations were within the range of 5–25 μg/L Pb and 1–5 μg/L Cd. – indicates value not determined. [b] PG = pyrolytically coated graphite, PGL = pyrolytically coated graphite with La treatment, PGM = pyrolytically coated graphite with Mo treatment (*5*), PGML = pyrolytically coated graphite with Mo treatment followed by a La treatment.

suggested that the addition of lanthanum to the system may help suppress interferences in certain matrices. For catfish digests, formation of a relatively smooth atomization peak was observed for lead using a lanthanum treated tube. The uncompensated background signal appeared sufficiently separated from the lead atomization peak. However, with the addition of small amounts of lanthanum to the solution, the percent recovery of standard additions into this matrix was low (Table II, No. 3). Furthermore, repeatedly injecting solutions into the furnace containing relatively high lanthanum concentrations tended to contribute to a more rapid degradation of the tube, owing to the formation of lanthanum carbide and its subsequent reactivity with the injected aqueous acidic samples.

The high stability of molybdenum treated tubes noted by other workers (*5*) was also observed in this work. This is probably a reflection of molybdenum forming a highly stable interstitial carbide. Since molybdenum and lanthanum improved lead atomization in this matrix, it appeared possible that a molybdenum treated tube subjected to a lanthanum treatment might be sufficiently stable and provide a well formed peak for lead in tissue digests. Thus, several lanthanum injection (50 μL of 5% La) and atomization sequences were applied to a molybdenum treated tube. After sufficient tube conditioning, the shape of the lead signal (Figure 2B) for a sample of digest changed to a single smooth peak and, over long-term use, the tube appeared to be reasonably stable. In addition, the uncompensated background signal appeared reduced and sufficiently separated from the lead peak.

Uncompensated background signals did not appear significant for cadmium atomization peaks using either a graphite tube or a pyrolytic graphite tube treated with molybdenum and lanthanum (Figure 3). Moreover, it is seen from using the latter conditions that the background signal is also of less magnitude and more separated in time from the cadmium absorption peak.

Chemical Interferences. Table II characterizes the degree to which chemical interferences exist in a catfish matrix, particularly for lead, as a function of using various types of treated graphite tubes and matrix modifying reagents. Intercomparisons were made using the same sample matrix concentration. The injected calcium, magnesium, sodium, and potassium concentrations were approximately 25% of each value previously measured for digests. Recovery values were the mean of several determinations on well conditioned newly prepared tubes. Perhaps the greatest interference observed

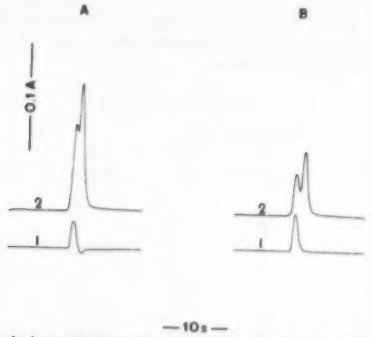

Figure 3. Cadmium atomization signal shape of a whole catfish tissue digest. (A) Graphite tube, (B) molybdenum and lanthanum treated pyrolytic graphite tube. Curves: (1) with D_2 background correction, (2) without D_2 background correction. Added background matrix: (A) 1% v/v $HClO_4$; (B) 1% v/v $HClO_4$, 6% w/v ammonium nitrate; 100 mg/L Mo, 500 mg/L La. Atomization settings: 2500 °C, 10 s, 4-s ramp

was with no reagent additions and using a pyrolytically coated graphite tube (Table II, No. 1); the recovery of 10 μg/L lead added to a sample of digest was irreproducible and less than 10%. For cadmium, however, reproducibility and recovery were considerably better for these conditions. Although addition of 6% ammonium nitrate to the solution increased the lead recovery to only 13% (No. 2), it was still added in the following experiments because of its acceptance as a matrix modifying reagent for salt-type matrices. With lanthanum also added to the system (No. 3), the recovery improved considerably. However, it was only after treating a tube with molybdenum that the recovery rose to an acceptable level (No. 4). Addition of 100 mg/L of molybdenum (No. 5) to the solution appeared to effect little change in recovery, although it has been implied that the addition of molybdenum to solutions may improve long-term stability of the tube (2). Therefore, experiments were generally performed with the molybdenum addition. Treating a pyrolytically coated graphite tube with molybdenum and subsequently lanthanum and adding lanthanum or both lanthanum and molybdenum to the solution provided both good recoveries of lead and cadmium (Nos. 6–8) and well formed atomization peaks. If tubes were not adequately coated with pyrolytic graphite prior to the molybdenum and lanthanum treatment or if highly acidic samples were injected, unstable results were obtained.

Molybdenum and lanthanum treated pyrolytic graphite tubes were also characterized by determining the degree of chemical interference from a few relatively simple and common inorganic salts. The percent recovery of standard amounts of lead (10–25 μg/L) added to solutions containing $MgCl_2$ or $Ca(ClO_4)_2$ was determined, relative to identical standards without these salts present. The determined mean recovery values were: 92% (0.1% w/v $MgCl_2$), 98% (0.2% w/v $Ca(ClO_4)_2$), and 90% (1% w/v $Ca(ClO_4)_2$). Similarly, the recoveries for cadmium (2–5 μg/L) were: 91% (0.1% w/v $MgCl_2$) and 97% (0.2% w/v $Ca(ClO_4)_2$). Appropriate corrections were made for any observed blanks and both the graphite tube and solutions were prepared as previously given under Experimental. These results indicated that a mean percent recovery of 90% or better could be obtained under conditions where the concentration of either calcium or magnesium was much greater than that encountered in digests, even for magnesium chloride media, often considered to be one of the most troublesome salts.

Routine Results. Table III summarizes the mean recoveries obtained for a number of routine analyses using conditions given for case No. 7 in Table II in addition to the mean residue concentrations. The residue values do not represent replicates, but serve only to indicate the general concentration level determined. For all tissue types, the mean percent recovery varied from 91% to 100% for lead and 91%

Table III. Mean Analytical Recovery of Lead and Cadmium for Routine Residue Determinations

tissue type	no. of digests	mean residue, μg/g dry weight		mean % recovery[a]	
		Pb	Cd	Pb	Cd
NBS SRM 1577 bovine liver	3	0.33 (±0.01)[b]	0.31 (±0.05)	93 (±7)	91 (±10)
		0.34[c] (±0.08)	0.27[c] (±0.04)	--	--
whole catfish	42	0.26	0.039	93 (±6)	98 (±13)
whole bluegill	35	0.32	0.038	91 (±7)	107 (±5)
whole clam	31	0.83	1.30	100 (±6)	104 (±10)

[a] Recoveries for 5–25 μg/L Pb and 1–5 μg/L Cd. [b] Parentheses indicate standard deviation. [c] NBS certified value.

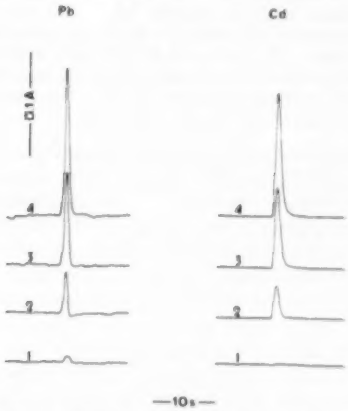

Figure 4. Typical atomization signal shapes for a (1) blank, (2) sample, (3) sample + 100 pg Pb + 10 pg Cd, and (4) sample + 200 pg Pb + 20 pg Cd

to 107% for cadmium. The means of triplicate analytical results for lead and cadmium in NBS SRM 1577 bovine liver were within the error limits of their reported true values. Typical lead and cadmium atomization signals for a blank, a sample, and a spiked sample are shown in Figure 4. Comparison of Figure 4 to Figure 2 shows that any apparent uncompensated background signals are effectively reduced using this tube with a short atomization ramp (internal gas stop mode) followed by a final atomization step with a 50 mL/min internal gas flow occurring just after appearance of the atomization peak.

Reproducibility, Detection Limit, and Accuracy. The typical relative standard deviation, obtained from ten repetitive injections of a spiked sample of digest, was 2.0% for lead and 2.7% for cadmium. The instrumental detection limits (2 standard deviation criteria) for lead and cadmium in digests were calculated to be 4 and 0.2 pg, respectively.

Several selected samples were analyzed both by the FAAS (Case No. 7, Table II) procedure and ASV (Table IV). In all cases, the method of standard additions was employed for calibration. The mean and relative deviation from the mean for duplicate determinations were calculated for ASV. For the FAAS procedure, the relative standard deviation of results from 7–8 different analytical runs on the same digests, performed before and after the ASV determinations, is correspondingly given. It is seen that the run-to-run variability is, understandably, slightly higher than the peak-to-peak injection reproducibility (2–3%) for a spiked sample of digest. Digests 1–5 were catfish and 6–10 were clams. Agreement of values between FAAS with the molybdenum and lanthanum treated tube and ASV generally appeared excellent. Among

Table IV. Comparison of FAAS and ASV Analytical Results for Fish and Clam Tissue Digests

	concentration, μg/L			
	Pb		Cd	
sample	FAAS	ASV	FAAS	ASV
1	2.4	2.5	0.40	0.36
	(14)[a]	(0.4)[b]	(5)	(10)
2	3.1	2.8	0.35	0.34
	(10)	(6)	(11)	(8)
3	2.5	2.5	0.43	0.30
	(10)	(2)	(8)	(0.5)
4	3.3	3.2	0.40	0.39
	(12)	(3)	(5)	(4)
5	2.2	2.7	0.46	0.45
	(11)	(13)	(8)	(1)
6	1.7	0.7	2.3	1.9
	(26)	(8)	(14)	(10)
7	2.4	0.6	1.9	1.4
	(46)	(24)	(6)	(16)
8	1.3	1.0	1.7	1.7
	(26)	(31)	(6)	(19)
9	1.5	1.4	1.1	1.0
	(18)	(0)	(5)	(1)
10	0.9	0.9	2.0	2.3
	(32)	(5)	(10)	(4)

[a] % relative standard deviation for 7–8 determinations. [b] % relative deviation from mean for duplicate determinations.

the cadmium values, the most significant differences, although small, occurred with samples 3 and 7. However, for numbers 6 and 7 for lead, the ASV values were distinctly lower than the FAAS values. Even though sedimentary material was not visibly apparent in the digest, the presence of analyte associated with particulates in these two clam samples may explain such differences, since ASV values should correspond only to the dissolved fraction. But this possibility could not be tested since there was insufficient sample remaining to perform additional experiments. In support of this possibility, however, the work of Agemian and Chau (*21*) provided some data on metal recovery from sediments using an HNO_3–$HClO_4$ digestion procedure. They observed that an HNO_3–$HClO_4$–HF digestion procedure gave substantially higher values than the HNO_3–$HClO_4$ procedure. Since the presence of sedimentary material in clam tissue digest is probable, it is entirely possible, based on this work, that the differences observed between the FAAS and ASV values for these samples may be explained on this basis.

In summary, background, chemical, or peak shape interferences in the determination of lead and cadmium in nitric–perchloric acid digests of whole fish and clam tissues can be suppressed by using the procedure described. In addition, preliminary evidence suggests that other elements might be similarly determined. The molybdenum and lanthanum treatment may provide a useful alternative to using other types of treated graphite atomizers or relatively tedious and labor intensive procedures.

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